Curvature Corrections to Surface Tension

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Abstract. The paper studies the size dependence of the surface tension at a weakly curved liquid-vapor interface. Statistical expressions for the first and the second correction to the surface tension are derived with the use of expansion of the first of the equations of the hierarchy of Born-Green-Yvon into a series in terms of the curvature of the dividing surface. A method of approximate evaluation of the second correction by information on the properties of a planar liquid-vapor interface is suggested.

Keywords: Pure, vapour-liquid equilibria, interfacial tension, Statistical mechanics, molecular simulation

Introduction

The problem of dependence of the surface tension σ of vapor bubbles and liquid droplets on the radius of curvature of the dividing surface R is the subject of numerous theoretical [1 – 6] and experimental [7 – 10] investigations. The variety of approaches and methods has not yet yielded unanimity even in concepts of the qualitative character of this dependence. For an interface curved sufficiently weakly the size dependence of the surface tension may be presented as follows [4]

$$\sigma(J,K) = \sigma_0 + kC_0\,J + kJ^2/2 + \hat{k}\,K \ . \tag{1}$$

where σ_0 is the surface tension of a planar interface, C_0 is the spontaneous curvature, k is the rigidity constant of bending and $\hat{k}$ is the rigidity constant associated with the Gaussian curvature, $J = c_x + c_y$ is the total curvature, and $K = c_x c_y$ is the Gaussian curvature.

A peculiar role in physics of surface phenomena is played by spherically symmetric surfaces. Since a sphere has the smallest area at a given volume, it is the equilibrium form for a gas bubble or a liquid droplet surrounded by some other fluid phase. Spherical symmetry is characteristic of critical nuclei from which the phase transition of the first kind starts in isotropic systems. In connection with the great significance of spherical surfaces we will restrict our consideration in this paper just to this case. For a spherical interface $c_x = c_y = c = 1/R$ (following Blokhuis and Bedeaux we will take R to mean the radius of an equimolar dividing surface), and consequently, $J = 2/R$, $K = 1/R^2$, and Expression (1) reduces to

$$\sigma(R) = \sigma_0 + \sigma_1/R + \sigma_2/R^2 \ , \qquad \sigma_1 = 2kC_0 \ , \qquad \sigma_2 = 2k + \hat{k} \ .$$

Thermodynamic analysis of the size dependence of the surface tension in the case of a spherical surface leads to the well-known differential equation [11]

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$$\left(\frac{d\ln\sigma_*}{d\ln c_*}\right)_T=\left(\frac{d\ln\sigma}{d\ln c}\right)_T=\frac{-2\delta c_*\left[1+\delta c_*+\delta^2c_*^2/3\right]}{1+2\delta c_*\left[1+\delta c_*+\delta^2c_*^2/3\right]},\qquad c_*=\frac{1}{R_*},\tag{2}$$

which makes it possible to relate corrections to the surface tension with Tolman's length

$$\delta=R-R_*$$

where the subscript "*" denotes the quantities pertaining to the surface tension. The latter is determined by Laplace's equation

$$p_\alpha-p_\beta=2\sigma_*/R_*,$$

where p is the pressure, the subscript "α" refers to the inner phase with respect to the curved surface, "β" to the other one. According to Expression (2)

$$\sigma_1=-2\sigma_0\delta_0,\qquad \sigma_2=\sigma_0\left(2\delta_0^2-\delta_1\right),\tag{3}$$

where δ_0 and δ_1 are the coefficients of expansion of the Tolman's length in terms of curvature

$$\delta=\delta_0+\delta_1/R+\cdots.$$

Any further determination of the Tolman's length and corrections to the surface tension is beyond the scope of purely phenomenological consideration and requires a statistical approach.

Recently, by calculating the increment of the canonical partition function of a two-phase system with a curved interface caused by two independent deformations, Blokhuis and Bedeaux [4] managed to obtain expressions relating curvature corrections to the surface tension with the intermolecular potential $\phi(r)$ and the pair density of the interface. In the context of the approach suggested by them the authors [4] obtained for the surface tension of a planar interface σ_0 the well-known result of Kirkwood and Buff [12]

$$\sigma_0=\frac{1}{4}\int dz_1\int d\vec{r}_{12}\,\phi'(r)r\left(1-3s^2\right)\rho_0^{(2)}(z_1,z_2,r),\tag{4}$$

for the first curvature correction on a spherical surface σ_1 two equivalent expressions

$$\sigma_1=\frac{1}{4}\int dz_1\int d\vec{r}_{12}\,\phi'(r)r\left(1-3s^2\right)(z_1+z_2)\rho_0^{(2)}(z_1,z_2,r),\tag{5}$$

$$\sigma_1=\frac{1}{4}\int dz_1\int d\vec{r}_{12}\,\phi'(r)r\left(1-3s^2\right)\rho_1^{(2)}(z_1,z_2,r),\tag{6}$$

and for the second correction σ_2 relations

$$\sigma_2=\frac{1}{4}\int dz_1\int d\vec{r}_{12}\,\phi'(r)r\left[\left(1-3s^2\right)\frac{z_1+z_2}{2}\rho_1^{(2)}-\frac{r^2s^2}{6}\left(3-5s^2\right)\rho_0^{(2)}\right],\tag{7}$$

$$\sigma_2=\frac{1}{4}\int dz_1\int d\vec{r}_{12}\,\phi'(r)r\left[\left(1-3s^2\right)\left(\rho_2^{(2)}+z_1z_2\rho_0^{(2)}\right)+\frac{r^2s^2}{3}\left(3-5s^2\right)\rho_0^{(2)}\right],\tag{8}$$

In the expressions presented the values of coordinates z are counted off from the position z_e of the equimolar dividing surface, $r=\left|\vec{r}_{12}\right|$, $\rho_i^{(2)}$ are the coefficients of expansion of the pair density of the curved interface

$$\rho^{(2)}(\vec{r}_1,\vec{r}_2)=\rho_0^{(2)}(z_1,z_2,r)+\rho_1^{(2)}(z_1,z_2,r)/R+\rho_2^{(2)}(z_1,z_2,r)/R^2+\cdots,\tag{9}$$

the product sr is the projection of the vector $\vec{r}_{12}$ on the direction of the vector $\vec{r}_1$.

The results obtained by Blokhuis and Bedeaux enabled one for the first time to calculate rigorously the value of the first correction σ_1 to the surface tension in the Lennard–Jones fluid [13, 14]. As is shown by these rigorous calculations, and also by earlier evaluations in the framework of the method of the density functional [15] or the van der Waals capillarity theory [6], the absolute value of the parameter δ_0 determining according to (3) the value of σ_1 is only tenth fractions of the molecular diameter. Rigorous calculation of the second correction σ_2 by formulae (7), (8) is hampered by the fact that for their use information on the properties of a planar liquid-vapor interface is not sufficient, and some extremely cumbersome and problematic numerical experiments [14] on simulation of curved surfaces are required. The result obtained in this case proves to be comparable with its error. At the same time, owing to the extremely infinitesimal value of the first correction information on the value of σ_2 may turn out to be necessary for correct description of the surface tension even for sufficiently weakly curved interfaces. Thus for instance, as is shown by investigations [6, 16, 17], the value of the second correction to the surface tension is necessary and sufficient for correct interpretation of experiments on the boiling-up kinetics of pure fluids and their solutions in the framework of the homogeneous nucleation theory. In this connection the search for alternative expressions for the second correction becomes highly topical. To solve this problem we use the first of the equations of the BGY hierarchy.

Expansion of the First of the Equations of the BGY Hierarchy in Terms of Curvature

In the general case the first of the equations of the BGY hierarchy (Born–Green–Yvon) [11] will look like:

$$\nabla\rho(\vec{r}) = \frac{1}{k_B T}\int d\vec{r}_2 \frac{\vec{r}_{12}}{r_{12}}\phi'(r)\rho^{(2)}(\vec{r}_1,\vec{r}_2). \tag{10}$$

As applied to a spherically symmetric system this equation reduces to

$$\frac{\partial\rho(r_1)}{\partial r_1} = \frac{2\pi}{k_B T}\int_0^\infty r^2 dr \int_{-1}^{1} ds\, s\phi'(r)\rho^{(2)}(r_1,r_2,r), \tag{11}$$

where $s = \cos\theta_{12}$, θ_{12} is the angle between $\vec{r}_1$ and $\vec{r}_{12}$, r_1 and r_2 are the distances from the first and the second particles to the center of the sphere.

Now, by assuming the surface curvature to be weak and the expansion (9) to be legitimate, we will expand the written equation into a series in terms of curvature keeping the terms up to the 3-order infinitesimal ($\sim R^{-3}$). This expansion is similar to the expansions of integrals described by Blokhuis and Bedeaux in Appendix A of ref. [4].

The value of $r_2 = |\vec{r}_2|$ is determined by the values of r_1, s and r:

$$r_2 = \sqrt{r_1^2 + 2r_1 sr + r^2},$$

whence up to the terms of the third order in terms of (r/r_1) we have

$$\Delta r = r_2 - r_1 - sr = \frac{1-s^2}{2}\frac{r^2}{r_1}\left[\left(1-\frac{sr}{r_1}\right)+\frac{1}{4}\frac{r^2}{r_1^2}\left(5s^2-1\right)\right].$$

Now we expand the function $\rho^{(2)}\left(r_1,r_2,r\right)$ in the vicinity of $\rho^{(2)}\left(r_1,r_1+sr,r\right)$

$$\rho^{(2)}\left(r_1,r_2,r\right)=\left[1+\frac{\Delta r}{r}\frac{\partial}{\partial s}+\frac{1}{2}\frac{\left(\Delta r\right)^2}{r^2}\frac{\partial^2}{\partial s^2}+\frac{1}{6}\frac{\left(\Delta r\right)^3}{r^3}\frac{\partial^3}{\partial s^3}\right]\rho^{(2)}\left(r_1,r_1+sr,r\right).$$

By substituting the written expansions into (11) we have

$$\frac{\partial\rho\left(r_1\right)}{\partial r_1}=\frac{2\pi}{k_BT}\int_0^\infty dr\,\phi'\left(r\right)r^2\int_{-1}^{1}ds\left[s+\frac{sr}{2r_1}\left(1-s^2\right)\left(1-\frac{sr}{r_1}+\frac{5s^2-1}{4}\frac{r^2}{r_1^2}\right)\left(\frac{\partial}{\partial s}\right)\right.$$
$$\left.+\frac{s\left(1-s^2\right)^2r^2}{8r_1^2}\left(1-\frac{2sr}{r_1}\right)\left(\frac{\partial^2}{\partial s^2}\right)+\frac{s\left(1-s^2\right)^3r^3}{48r_1^3}\left(\frac{\partial^2}{\partial s^2}\right)\right]\rho^{(2)}\left(r_1,r_1+sr,r\right).$$

Integrating by parts the term that contains the third derivative with respect to s we obtain

$$\frac{\partial\rho\left(r_1\right)}{\partial r_1}=\frac{2\pi}{k_BT}\int_0^\infty dr\,\phi'\left(r\right)r^2\int_{-1}^{1}ds\left[s+\frac{sr}{2r_1}\left(1-s^2\right)\left(1-\frac{sr}{r_1}+\frac{5s^2-1}{4}\frac{r^2}{r_1^2}\right)\left(\frac{\partial}{\partial s}\right)\right.$$
$$\left.+\frac{\left(1-s^2\right)^2r^2}{8r_1^2}\left(s-\frac{5s^2+1}{6}\frac{r}{r_1}\right)\left(\frac{\partial^2}{\partial s^2}\right)\right]\rho^{(2)}\left(r_1,r_1+sr,r\right).$$

Integrating similarly the term with the second derivative with respect to s we come to

$$\frac{\partial\rho\left(r_1\right)}{\partial r_1}=\frac{2\pi}{k_BT}\int_0^\infty dr\,\phi'\left(r\right)r^2\int_{-1}^{1}ds\left[s\rho^{(2)}\left(r_1,r_1+sr,r\right)+\frac{1-s^2}{2}\frac{r}{r_1}\left(s-\frac{1-s^2}{4}\frac{r}{r_1}\right)\frac{\partial\rho^{(2)}}{\partial s}\right].$$

It should be noted that despite the disappearance in the last expression of the terms proportional to $\left(r/r_1\right)^3$ calculations are made with an accuracy of the third order. At last, by performing the last integration by parts, we finally obtain

$$\frac{\partial\rho\left(r_1\right)}{\partial r_1}=\frac{2\pi}{k_BT}\int_0^\infty dr\,\phi'\left(r\right)r^2\int_{-1}^{1}ds\left[s-\frac{1-3s^2}{2}\frac{r}{r_1}-\frac{s}{2}\left(1-s^2\right)\frac{r^2}{r_1^2}\right]\rho^{(2)}\left(r_1,r_1+sr,r\right).\qquad(12)$$

Let us denote the distance from the point $\vec{r}_1$ to the dividing surface R along the normal by $z_1=r_1-R$. Passing now from the expansion in terms of $1/r_1$ to the expansion in terms of $1/R$:

$$\frac{1}{r_1}=\frac{1}{R}\left(1-\frac{z_1}{R}+\frac{z_1^2}{R^2}-\cdots\right),$$

we transform Relation (12) to

$$\frac{\partial\rho\left(r_1\right)}{\partial r_1}=\frac{2\pi}{k_BT}\int_0^\infty dr\,\phi'\left(r\right)r^2\int_{-1}^{1}ds\left\{s-\frac{1-3s^2}{2}\frac{r}{R}+\left[z_1\left(1-3s^2\right)-sr\left(1-s^2\right)\right]\frac{r}{2R^2}\right.$$
$$\left.+\left[sr\left(1-s^2\right)-\frac{z_1}{2}\left(1-3s^2\right)\right]\frac{rz_1}{R^3}\right\}\rho^{(2)}\left(r_1,r_1+sr,r\right).\qquad(13)$$

It should be mentioned that in the expression presented the pair density $\rho^{(2)}\left(r_1,r_1+sr,r\right)$ and the particle density $\rho\left(r_1\right)$ are the functions of distribution of a curved interface and characterize the distribution of particles at the points located at distances z_1 and z_1+sr along the normal from the equimolar surface. Just as the surface tension at a curved surface may differ from its planar limit σ_0, the functions $\rho^{(2)}$ and $\rho(r_1)$ may differ from the corresponding functions of a planar interface. By using Expansion (9) for the pair density and a similar expansion for the particle density

$$\rho(r_1) = \rho_0(z_1) + \rho_1(z_1)/R + \rho_2(z_1)/R^2 + \cdots, \tag{14}$$

we obtain in Relation (13) in the zero order in terms of $(1/R)$:

$$k_B T \frac{\partial \rho_0(z_1)}{\partial z_1} = \int d\vec{r}\, \phi'(r) s \rho_0^{(2)}(z_1, z_1 + sr, r), \tag{15}$$

in the first order

$$k_B T \frac{\partial \rho_1(z_1)}{\partial z_1} = \int d\vec{r}\, \phi'(r) \left[s\rho_1^{(2)} - \frac{1-3s^2}{2} r \rho_0^{(2)} \right], \tag{16}$$

in the second order

$$k_B T \frac{\partial \rho_1(z_1)}{\partial z_1} = \int d\vec{r}\, \phi'(r) \left[s\rho_2^{(2)} - \frac{1-3s^2}{2} r \rho_1^{(2)} + \left[z_1 \left(1-3s^2\right) - sr\left(1-s^2\right)\right] \frac{r}{2} \rho_0^{(2)} \right], \tag{17}$$

and in the third order

$$\begin{aligned} k_B T \frac{\partial \rho_3(z_1)}{\partial z_1} = \int d\vec{r}\, \phi'(r) \Bigg\{ & s\rho_3^{(2)} - \frac{1-3s^2}{2} r \rho_2^{(2)} + \left[z_1 \left(1-3s^2\right) - sr\left(1-s^2\right)\right] \frac{r}{2} \rho_1^{(2)} \\ & + \left[sr\left(1-s^2\right) - \frac{z_1}{2}\left(1-3s^2\right)\right] r z_1 \rho_0^{(2)} \Bigg\}. \end{aligned} \tag{18}$$

If Eq. (15) is nothing but Equation of BGY (10) written as applied to a planar interface, the deduced equations (16) – (18) are new relations which relate to each other different coefficients of expansions of the pair (9) and the particle (14) densities. In the next part we shall use these relations to derive statistical expressions for the first and the second curvature correction to the surface tension.

Application of the Relation Obtained to the Problem of Size Dependence of the Surface Tension

Integration of the obtained relations (15) – (18) with respect to z_1 from the point z_α, where the homogeneity of the phase α is achieved, to the corresponding point z_β in the second phase gives

$$k_B T \left(\rho_{\alpha,0} - \rho_{\beta,0}\right) - \frac{1}{6} \int d\vec{r}\, \phi'(r) r \left[\rho_{\alpha,0}^{(2)}(r) - \rho_{\beta,0}^{(2)}(r) \right] = 0, \tag{19}$$

$$\begin{aligned} k_B T \left(\rho_{\alpha,1} - \rho_{\beta,1}\right) - \frac{1}{6} \int d\vec{r}\, \phi'(r) r \left[\rho_{\alpha,1}^{(2)}(r) - \rho_{\beta,1}^{(2)}(r) \right] = \\ \frac{1}{2} \int_{z_\alpha}^{z_\beta} dz_1 \int d\vec{r}\, \phi'(r) r \left(1-3s^2\right) \rho_0^{(2)}, \end{aligned} \tag{20}$$

$$k_BT\left(\rho_{\alpha,2}-\rho_{\beta,2}\right)-\frac{1}{6}\int d\vec{r}\,\phi'(r)\,r\left[\rho^{(2)}_{\alpha,2}(r)-\rho^{(2)}_{\beta,2}(r)\right]=$$
$$\frac{1}{2}\int_{z_\alpha}^{z_\beta}dz_1\int d\vec{r}\,\phi'(r)\,r\left(1-3s^2\right)\rho_1^{(2)}-\frac{1}{2}\int_{z_\alpha}^{z_\beta}dz_1\int d\vec{r}\,\phi'(r)\,r\left[z_1\left(1-3s^2\right)-sr\left(1-s^2\right)\right]\rho_0^{(2)}\ , \tag{21}$$

$$k_BT\left(\rho_{\alpha,3}-\rho_{\beta,3}\right)-\frac{1}{6}\int d\vec{r}\,\phi'(r)\,r\left[\rho^{(2)}_{\alpha,3}(r)-\rho^{(2)}_{\beta,3}(r)\right]=$$
$$\frac{1}{2}\int_{z_\alpha}^{z_\beta}dz_1\int d\vec{r}\,\phi'(r)\,r\left(1-3s^2\right)\rho_2^{(2)}-\frac{1}{2}\int_{z_\alpha}^{z_\beta}dz_1\int d\vec{r}\,\phi'(r)\,r\left[z_1\left(1-3s^2\right)-sr\left(1-s^2\right)\right]\rho_1^{(2)} \tag{22}$$
$$-\int_{z_\alpha}^{z_\beta}z_1dz_1\int d\vec{r}\,\phi'(r)\,r\left[sr\left(1-s^2\right)-\frac{z_1}{2}\left(1-3s^2\right)\right]\rho_0^{(2)}\ ,$$

In deriving (19) – (22) use was made of the transformation of integrals $L_{0,i}$ (see Appendix, Eqs. (32), (33))

$$L_{0,i}=\int_{z_\alpha}^{z_\beta}dz_1\int d\vec{r}\,\phi'(r)\,s\rho_i^{(2)}=-\frac{1}{6}\int d\vec{r}\,\phi'(r)\,r\left[\rho^{(2)}_{\alpha,i}(r)-\rho^{(2)}_{\beta,i}(r)\right].$$

Next it should be noted that according to the statistical determination of pressure in a homogeneous fluid

$$p(\rho)=\rho k_BT-\frac{1}{6}\int d\vec{r}\,\phi'(r)\,r\rho^{(2)}(r) \tag{23}$$

the coefficients of expansion of the pressure difference $\left(p_\alpha-p_\beta\right)$ are written at the left of Eqs. (19 – (22)

$$p_\alpha-p_\beta=\left(p_\alpha-p_\beta\right)_0+\left(p_\alpha-p_\beta\right)_1\Big/R+\left(p_\alpha-p_\beta\right)_2\Big/R^2+\cdots. \tag{24}$$

On the other hand, the pressure difference in coexistent phases is connected with the surface tension through Laplace's equation, which for an equimolar dividing surface takes the form:

$$p_\alpha-p_\beta=\frac{2\sigma}{R}+\left[\frac{d\sigma}{dR}\right]=\frac{2\sigma_0}{R}+\frac{\sigma_1}{R^2}+\frac{0}{R^3}\ , \tag{25}$$

where the well-known [11] equality of derivatives is used

$$\left[\frac{d\sigma}{dR}\right]=\left(\frac{\partial\sigma}{\partial R}\right)_T=-\frac{\sigma_1}{R^2}-\frac{2\sigma_2}{R^3}+\cdots.$$

When using (23), (24) and (25) we see that Expression (19) reduces to the equality of pressures above a planar interface, and Expressions (20) – (22) yield

$$2\sigma_0=\frac{1}{2}\int_{z_\alpha}^{z_\beta}dz_1\int d\vec{r}\,\phi'(r)\,r\left(1-3s^2\right)\rho_0^{(2)}\ ,$$

$$\sigma_1=\frac{1}{2}\int_{z_\alpha}^{z_\beta}dz_1\int d\vec{r}\,\phi'(r)\,r\left(1-3s^2\right)\rho_1^{(2)}-\frac{1}{2}\int_{z_\alpha}^{z_\beta}z_1dz_1\int d\vec{r}\,\phi'(r)\,r\left(1-3s^2\right)\rho_0^{(2)}$$
$$+\frac{1}{2}\int_{z_\alpha}^{z_\beta}dz_1\int d\vec{r}\,\phi'(r)\,r^2s\left(1-s^2\right)\rho_0^{(2)}\ ,$$

$$J_1 - J_2 = \int_{z_\alpha}^{z_\beta} dz_1 \int d\vec{r}\, \phi'(r) r^2 s\left(1-s^2\right) \rho_1^{(2)} - 2\int_{z_\alpha}^{z_\beta} z_1 dz_1 \int d\vec{r}\, \phi'(r) r^2 s\left(1-s^2\right) \rho_0^{(2)} + \int_{z_\alpha}^{z_\beta} z_1^2 dz_1 \int d\vec{r}\, \phi'(r) rs\left(1-3s^2\right) \rho_0^{(2)} , \tag{26}$$

where the following designations are introduced:

$$J_1 = \int_{z_\alpha}^{z_\beta} z_1 dz_1 \int d\vec{r}\, \phi'(r) r\left(1-3s^2\right) \rho_1^{(2)} , \qquad J_2 = \int_{z_\alpha}^{z_\beta} dz_1 \int d\vec{r}\, \phi'(r) r\left(1-3s^2\right) \rho_2^{(2)} .$$

The first of the obtained relations leads us to the well-known virial expression of Kirkwood and Buff (4). In the second expression, when transforming the last integral according to (see Appendix, Eqs. (32), (33))

$$\frac{1}{2}\int_{z_\alpha}^{z_\beta} dz_1 \int d\vec{r}\, \phi'(r) r^2 s\left(1-s^2\right) \rho_0^{(2)} = \int_{z_\alpha}^{z_\beta} dz_1 \int d\vec{r}\, \phi'(r) r^2 s\left(1-3s^2\right) \rho_0^{(2)} .$$

we see that it is a combination of the expressions (5) and (6) for the coefficient σ_1.

The last of the obtained expressions (26) does not contain any information on the second correction to the surface tension as the terms of the third order in Relation (25) cancel out, but it contains the same integrals as Eqs. (7), (8), which determine the value of σ_2. By subtracting (8) from (7) we come to

$$J_1 - J_2 = \frac{1}{2}\int_{z_\alpha}^{z_\beta} dz_1 \int d\vec{r}\, \phi'(r) r^3 s^2 \left(3-5s^2\right) \rho_0^{(2)} + \int_{z_\alpha}^{z_\beta} dz_1 \int d\vec{r}\, \phi'(r) r\left(1-3s^2\right) z_1 z_2 \rho_0^{(2)} - \frac{1}{2}\int_{z_\alpha}^{z_\beta} dz_1 \int d\vec{r}\, \phi'(r) r^2 s\left(1-3s^2\right) \rho_1^{(2)} ,$$

Comparison of the last relation with (26) with allowance for the transformation of integrals (Appendix, Eqs. (34), (35)) shows that Relation (26) is in complete agreement with statistical expressions for the second curvature correction to the surface tension. Hence the obtained result (26) may be regarded as confirmation of the equivalency of Eqs. (7) and (8).

Besides the confirmation of statistical expressions (4) – (8) Relations (16) – (18) derived in the previous part may be used for obtaining additional information on the integrals determining the second correction σ_2. For further analysis we shall expand into a series in terms of the curvature of the dividing surface the relation determining the equimolar radius

$$\int_0^\infty r^2 \left(\rho(r) - \rho_{\alpha\beta}\right) dr = 0 , \qquad \rho_{\alpha\beta} = \begin{cases} \rho_\alpha , & r < R , \\ \rho_\beta , & r > R . \end{cases}$$

Using (14) and passing on to the variable $z = r - R$, we have

$$\int_{-\infty}^{\infty} \left(1 + \frac{2z}{R} + \frac{z^2}{R^2}\right)\left[\left(\rho_0 - \rho_{\alpha\beta,0}\right) + \frac{\rho_1 - \rho_{\alpha\beta,1}}{R} + \frac{\rho_2 - \rho_{\alpha\beta,2}}{R^2} + \frac{\rho_3 - \rho_{\alpha\beta,3}}{R^3}\right] dz .$$

By assembling the terms at the same degrees of $(1/R)$ in the zero order we obtain the determination of the equimolar surface at a planar interface

$$\int z\left(\frac{d\rho_0}{dz}\right)dz = 0\,,$$

in the first order

$$\int z\left(\frac{d\rho_1}{dz}\right)dz = -\int z^2\left(\frac{d\rho_0}{dz}\right)dz\,,$$

and in the second order

$$\int z\left(\frac{d\rho_2}{dz}\right)dz = -\frac{1}{3}\int z^3\left(\frac{d\rho_0}{dz}\right)dz - \int z^2\left(\frac{d\rho_1}{dz}\right)dz\,.$$

With allowance for the relations obtained it can be shown that additional multiplication of Eq. (15) by z_1 and integration give

$$\int_{z_\alpha}^{z_\beta} z_1 dz_1 \int d\vec{r}\,\phi'(r)\,s\rho_0^{(2)} = 0\,. \tag{27}$$

Similarly, Eq. (16) leads to

$$k_B T\int z^2\left(\frac{d\rho_0}{dz}\right)dz = \int_{z_\alpha}^{z_\beta} z_1 dz_1 \int d\vec{r}\,\phi'(r)\,s\rho_1^{(2)} + \frac{1}{2}\int_{z_\alpha}^{z_\beta} z_1 dz_1 \int d\vec{r}\,\phi'(r)\,r\left(1-3s^2\right)\rho_0^{(2)}\,, \tag{28}$$

and Eq. (17) to

$$\begin{aligned} -\frac{k_B T}{3}\int z^3\left(\frac{d\rho_0}{dz}\right)dz - k_B T\int z^2\left(\frac{d\rho_1}{dz}\right)dz = \int_{z_\alpha}^{z_\beta} z_1 dz_1 \int d\vec{r}\,\phi'(r)\,s\rho_2^{(2)} - \frac{J_1}{2} \\ + \frac{1}{2}\int_{z_\alpha}^{z_\beta} z_1^2 dz_1 \int d\vec{r}\,\phi'(r)\,r\left(1-3s^2\right)\rho_0^{(2)} - \frac{1}{2}\int_{z_\alpha}^{z_\beta} z_1 dz_1 \int d\vec{r}\,\phi'(r)\,r^2 s\left(1-s^2\right)\rho_0^{(2)}\,. \end{aligned} \tag{29}$$

A relation for the second integral in the left side of Eq. (29) will be obtained by additional multiplication of Eq.(16) by z_1^2 and integration

$$k_B T\int z^2\left(\frac{d\rho_1}{dz}\right)dz = \int_{z_\alpha}^{z_\beta} z_1^2 dz_1 \int d\vec{r}\,\phi'(r)\,s\rho_1^{(2)} - \frac{1}{2}\int_{z_\alpha}^{z_\beta} z_1^2 dz_1 \int d\vec{r}\,\phi'(r)\,r\left(1-3s^2\right)\rho_0^{(2)}\,.$$

The last two relations make it possible to write for the integral J_1

$$J_1 = -\int_{z_\alpha}^{z_\beta} z_1 dz_1 \int d\vec{r}\,\phi'(r)\,r^2 s\left(1-s^2\right)\rho_0^{(2)} + \frac{2}{3}k_B T\int z^3\left(\frac{d\rho_0}{dz}\right)dz + 2I_1 + 2I_2\,, \tag{30}$$

where

$$I_1 = \int_{z_\alpha}^{z_\beta} z_1^2 dz_1 \int d\vec{r}\,\phi'(r)\,s\rho_1^{(2)}\,, \qquad I_2 = \int_{z_\alpha}^{z_\beta} z_1 dz_1 \int d\vec{r}\,\phi'(r)\,s\rho_2^{(2)}\,.$$

The relation obtained for the integral J_1 determines the alternative means of calculating the second correction to surface tension. Combining (7), (30) with allowance for transformation of (32), (33) we get

$$\begin{aligned} \sigma_2 = -\frac{1}{4}\int_{z_\alpha}^{z_\beta} z_1 dz_1 \int d\vec{r}\,\phi'(r)\,r^2 s\left(1-s^2\right)\rho_0^{(2)} + \frac{1}{6}k_B T\int z^3\left(\frac{d\rho_0}{dz}\right)dz \\ + \frac{1}{60}\int d\vec{r}\,\phi'(r)\,r^3\left[\rho_{\alpha,1}^{(2)} - \rho_{\beta,1}^{(2)}\right] + 2I_1 + 2I_2\,, \end{aligned} \tag{31}$$

This expression, of course, is not simpler for calculating the second correction σ_2 than Expressions (7) and (8), but on its basis a new approximate evaluation of σ_2 may be suggested.

Relation (27) obtained earlier makes it possible to assume that the integrals I_1 and I_2 make a small contribution to Expression (31). If they are neglected, all the remaining terms in (31) may be determined on the basis of numerical experiments on simulation of two-phase systems with a planar interface and one-phase systems. Thus, for instance, the functions $\rho^{(2)}_{\alpha,1}$, $\rho^{(2)}_{\beta,1}$ determining the rate of change of the pair density in homogeneous phases may be expressed through the coefficients of expansion (14) for the particle density

$$\rho^{(2)}_{\alpha,1} = \left(\frac{d\rho^{(2)}_1}{d\rho}\right)_{\alpha,s} \rho_{\alpha,0}\ , \qquad \rho^{(2)}_{\beta,1} = \left(\frac{d\rho^{(2)}_1}{d\rho}\right)_{\alpha,s} \rho_{\beta,0}\ ,$$

where the subscript "s" denotes the state of equilibrium coexistence of phases (binodal). In their turn, the coefficients $\rho_{\alpha,1}$, $\rho_{\beta,1}$ are determined by the system of equations

$$\frac{1}{\rho_{\alpha,s}}\left(\frac{\partial p}{\partial \rho}\right)_{\alpha,s} \rho_{\alpha,1} = \frac{1}{\rho_{\beta,s}}\left(\frac{\partial p}{\partial \rho}\right)_{\beta,s} \rho_{\beta,1}\ ,$$

$$2\sigma_0 = \left(\frac{\partial p}{\partial \rho}\right)_{\alpha,s} \rho_{\alpha,1} - \left(\frac{\partial p}{\partial \rho}\right)_{\beta,s} \rho_{\beta,1}\ ,$$

the first of which follows from the condition of equality for the chemical potentials of phases, and the second from Laplace's equation (25).

Of course, generalization of the result (27) to the integrals I_1 and I_2 is no more than an assumption. Another assumption of the same kind for approximate evaluation of the second correction to the surface tension was made by Blokhuis and Bedeaux [4]. However, as distinct from the hypothesis adopted in Ref. [4], the legitimacy of our assumption may be checked indirectly owing to Relation (28). This relation contains an integral (the first on the right) of the intermediate type between the integral of Expression (27) and the integrals I_1 and I_2. Rigorous calculation in simulating the planar interfacial layer of the remaining terms in (28) will make it possible either to rule out or to indirectly confirm the above assumption.

Conclusion

The expansion of the first of the equations of the BGY hierarchy in terms of curvature has been studied in the framework of the investigation performed. A number of relations have been obtained for connecting the expansion coefficients of one- and two-particle distribution functions of an interfacial layer. These relations are used for analyzing the size dependence of the surface tension σ. It is shown that they are in complete agreement with the statistical expressions recently obtained for the first and the second curvature correction to σ. A new statistical expression for the second correction to the surface tension has been obtained. A method for approximate evaluation of the second correction on the basis of numerical experiments on simulation of two-phase system with a planar interface and one-phase system has been suggested.

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Appindix

When relations (15) – (16) are integrated with respect to z_1, the first integrals on the right take the form:

$$L_{0,i} = \int_{z_\alpha}^{z_\beta} dz_1 \int d\vec{r}\; f_r(r)\, f_s(s)\, \rho_i^{(2)}(z_1, z_1 + sr, r), \tag{32}$$

where $f_r(r)$ is an arbitrary function, $f_s(s)$ is an odd function s, i.e. $f_s(-s) = -f_s(s)$, $\rho_i^{(2)}$ is one of the expansion functions (9). For the first time a correct method of calculating an integral similar to (32) was demonstrated by Henderson [18]. On account of the odd character of the function $f_s(s)$, addition to the integrand of a constant has no effect on the value of the integral, and we can present integral (32) as follows:

$$L_{0,i} = 2\pi \int_0^\infty f_r(r) r^2 dr \int_{z_\alpha}^{z_\beta} dz_1 \int_{-1}^{1} ds\; f_s(s)\left[\rho_i^{(2)}(z_1, z_1 + sr, r) - \rho_{\alpha\beta,i}^{(2)}(z_1, z_e)\right],$$

where $\rho_{\alpha\beta,i}^{(2)} = \rho_{\alpha,i}^{(2)}$ at $z_1 < z_e$, and $\rho_{\alpha\beta,i}^{(2)} = \rho_{\beta,i}^{(2)}$ at $z_1 > z_e$. It is not difficult to notice that the pairs of particles for which $z_1 < 0$ and $z_2 < 0$ (or , on the contrary, $z_1 > 0$ and $z_2 > 0$) give no contribution to the integral in view of $\rho_i^{(2)}(z_1, z_2, r) = \rho_i^{(2)}(z_2, z_1, r)$. By keeping the pairs whose particles are on different sides of the dividing surface we obtain

$$L_{0,i} = 2\pi \int_0^\infty f_r(r) r^2 dr \left\{ \int_{-1}^{0} ds \int_0^{-sr} dz_1 f_s(s)\left[\rho_i^{(2)} - \rho_{\beta,i}^{(2)}\right] + \int_0^1 ds \int_{-sr}^{0} dz_1 f_s(s)\left[\rho_i^{(2)} - \rho_{\alpha,i}^{(2)}\right] \right\},$$

In the last expression the terms that contain the function $\rho_i^{(2)}(z_1, z_1 + sr, r)$ cancel too, and after some simple transformations we come to the desired result

$$L_{0,i} = -\frac{1}{2}\int d\vec{r}\; f_r(r) r\, f_s(s)\, s\left[\rho_{\alpha,i}^{(2)}(r) - \rho_{\beta,i}^{(2)}(r)\right]. \tag{33}$$

where at a given form of the function $f_s(s)$ integration with respect to s may be fulfilled. Thus, all the integrals $L_{0,i}$ may be determined by the properties of homogeneous phases $\rho_{\alpha,i}^{(2)}$ and $\rho_{\beta,i}^{(2)}$ in the vicinity of their equilibrium coexistence (binodal).

Now we shall snow the transformation of integral of the following type:

$$L_{1,i} = \int_{z_\alpha}^{z_\beta} z_1 dz_1 \int d\vec{r}\; f_r(r)\, f_s(s)\, \rho_i^{(2)}(z_1, z_1 + sr, r). \tag{34}$$

Using the relation

$$z_1 = (z_1 + z_2)/2 - sr/2,$$

we shall present (34) in the form of the sum of two integrals

$$L_{1,i} = -\frac{1}{2}\int_{z_\alpha}^{z_\beta} dz_1 \int d\vec{r}\; f_r(r)\, r\; f_s(s)\, s\left[\rho_i^{(2)}(z_1, z_1 + sr, r) - \rho_{\alpha\beta,i}^{(2)}\right]$$

$$+\frac{1}{2}\int_{z_\alpha}^{z_\beta} dz_1 \int d\vec{r}\; f_r(r)\; f_s(s)(z_1 + z_2)\left[\rho_i^{(2)}(z_1, z_1 + sr, r) - \rho_{\alpha\beta,i}^{(2)}\right].$$

By transforming the second integral on the right in the same way as (32) it is not difficult to show that it is equal to zero. Thus,

$$L_{1,i} = -\frac{1}{2}\int_{z_\alpha}^{z_\beta} dz_1 \int d\vec{r}\; f_r(r)\, r\; f_s(s)\, s\left[\rho_i^{(2)}(z_1, z_1 + sr, r) - \rho_{\alpha\beta,i}^{(2)}\right]. \qquad (35)$$

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